



## **MARKED-UP COPY OF SPECIFICATION**



## **NON-SINTERED ELECTRODE FOR AN ELECTROCHEMICAL GENERATOR CELL WITH AN ALKALINE ELECTROLYTE**

[01] The present invention relates to a non-sintered electrode such as that which is used in secondary electrochemical ~~generator~~cells with an alkaline electrolyte, such as for example: ~~nickel cadmium, nickel iron, nickel hydrogen, nickel hydrogen~~ fixing metal accumulators. It also covers the generator containing such an electrode nickel/cadmium, nickel/iron, nickel/hydrogen, and nickel/metal hydride storage cells. The invention also covers a cell containing such an electrode.

### **BACKGROUND OF THE INVENTION**

[02] There are several types of electrode, in particular sintered and non-sintered electrodes, also called pasted or plasticized electrodes. The electrodes most widely used today are of the non-sintered type. Compared with other electrodes, a non-sintered electrode contains a greater quantity of active material, its volume specific capacity is thus increased and its production cost lower.

[03] A non-sintered electrode consists of a support, serving as current collector, to which is applied a paste containing the active material and a binder, to which a conductive material is most often added. It is usually ~~carried out~~made by applying the paste in a porous three-dimensional conductive support such as a felt or a foam, made of metal or carbon. For reasons of cost, there is now a move towards the use of two-dimensional conductive supports. The known binders used to produce an electrode with a three-dimensional support prove unsuitable for a two-dimensional support.

[04] By way of example, patent application EP 0 750 358 describes for example a non-sintered nickel electrode the having a support of which is comprising a corrugated metal sheet wherein teeth have been formed in order

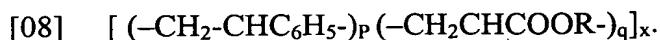
to fastenbind a microscopically irregularrough layer. A paste comprising carboxymethylcellulose (CMC) and a styrene/butadiene (SBR) copolymer is applied to this the layer. In this that case it was necessary to use a means other than the binder to ensure the mechanical behaviourstrength of the electrode,

[05] Also known is German patent application DE 19 709 107 which describes a nickel/metal hydride accumulatorstorage cell including an electrode formed from a paste applied to a substrate. The paste contains an acrylate binder having 6-to-5 carbon-ester groups with 6 to 15 carbon atoms.

### OBJECTS AND SUMMARY OF THE INVENTION

[06] The aim of the present invention is to propose an electrode, the mechanical behaviourpresenting mechanical strength and the mass specific capacity of whichthat are at least equivalent to those of an electrode having a three-dimensional current-collecting collector support.

[07] The subject of the present invention is provides a secondary electrochemical generatorcell, with an alkaline electrolyte, containing a non-sintered electrode comprising a two-dimensional conductive support covered by a layer containing an electrochemically active material and a binder, characterized in that thewherein said binder is a mixture of a cellulose compound and a styrene-acrylate copolymer of general formula:



[09] The styrene-acrylate copolymer is a combination of elementary styrene units  $(-CH_2-CHC_6H_5-)$ on the one hand, and of elementary acrylic ester or acrylate units  $(-CH_2CHCOOR-)$ on the other.

[10] The proportion of the sytrene-acrylate copolymer is preferably less than 4% by weight of the active layer. When the proportion of styrene-acrylate

copolymer is equal to or greater than 4% by weight of the active layer, the mass specific capacity of the electrode reduces perceptibly. In fact, an increase in the proportion of binder in the active layer means a reduction in the quantity of electrochemically active material, which causes a drop in performance-values.

[11] The proportion of styrene-acrylate copolymer is advantageously comprised betweenlies in the range of 0.15% and to 3% by weight of the active layer. A reduction in the quantity of binder to a value below 0.15% by weight of the active layer does not reduce the capacity, but the mechanical behaviourstrength of the electrode is degraded.

[12] The cellulose composition can be chosen in particular from methylcellulose (MC), carboxymethylcellulose (CMC), hydroxypropylmethyl-cellulose (HPMC), hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC). Carboxymethylcellulose (CMC) is further preferably used. The proportion of the cellulose compound is preferably comprised betweenlies in the range of 0.1 and to 1% by weight of the active layer.

[13] According toIn a particular embodiment of the present invention, the electrochemically active material comprises a nickel hydroxide. This hydroxide preferably has a spheroidal shape and has a grain size comprised between 7  $\mu\text{m}$  and 20  $\mu\text{m}$  lying in the range 7  $\mu\text{m}$  to 20  $\mu\text{m}$ .

[14] It is understood that the term "electrochemically active material containing nickel hydroxide" as used in the present application canmay mean a nickel hydroxide, a hydroxide containing principally nickel, but also a nickel hydroxide containing at least one syncrystallized hydroxide of an element chosenselected from zinc, cadmium, and magnesium, and at least one syncrystallized hydroxide of an element chosen from cobalt, manganese, aluminium, yttrium,

calcium, strontium, zirconium, and copper. A syncrystallized hydroxide contained in the nickel hydroxide is a hydroxide forming a solid solution with the nickel hydroxide, i.e. occupying, in continuously variable proportion, the atomic sites defined by the crystal lattice of the nickel hydroxide.

[15] The active material can be covered by a coating based on cobalt oxide or hydroxide optionally containing other elements such as nickel, zinc, aluminum, and/or manganese, or else by a porous metal coating, of nickel for example.

[16] Nickel hydroxide is a ~~not very poorly~~ conductive compound which ~~necessitates~~needs ~~the~~ a addition of a conductive material ~~to be added to permit~~ permitting a good electric percolation. The active layer also contains a conductive material ~~chosenselected~~ from conductive particles, conductive fibresfibers, and their mixtures thereof. The conductive particles ~~ear~~may be ~~chosenselected~~ from carbon particles, metal particles, such as nickel for example, or the powder of a compound of a transition metal such as for example Co, CoO, Co(OH)<sub>2</sub>, the ~~mixed~~composite oxide of lithium and cobalt LiCoO<sub>2</sub> and an oxide of conductive cobalt of a valency greater than 2. ~~The said~~Said conductive fibresfibers are ~~chosenselected~~ from carbon fibresfibers, metal fibresfibers, or fibresfibers covered with metal, such as nickel for example.

[17] The active layer preferably contains a conductive compound constituted essentially by a compound of cobalt, preferably metal cobalt Co, cobalt oxide CoO, cobalt hydroxide Co(OH)<sub>2</sub>, the ~~mixed~~composite oxide of lithium and cobalt LiCoO<sub>2</sub> or an oxide of conductive cobalt of a valency greater than 2.

[18] The proportion of the conductive material in the active layer is advantageously ~~between~~lies in the range of 3% ~~and~~to 15% by weight of the layer.

Beyond this value, the volumetric volume specific capacity of the electrode decreases because of the proportional reduction in the quantity of active material.

[19] The active layer ~~can~~may also contain at least one other compound ~~chosen~~selected from the compounds of zinc such as ZnO or Zn(OH)<sub>2</sub>, of yttrium such as Y<sub>2</sub>O<sub>3</sub> or Y(OH)<sub>3</sub>, ytterbium such as Yb<sub>2</sub>O<sub>3</sub> or Yb(OH)<sub>3</sub>, and calcium such as CaO, Ca(OH)<sub>2</sub> or CaF<sub>2</sub>. This compound is usually added in powder form.

[20] ~~According to~~In a first variant, the layer also contains a powder of a compound of yttrium, preferably yttrium oxide Y<sub>2</sub>O<sub>3</sub> or yttrium hydroxide Y(OH)<sub>3</sub>.

[21] ~~According to~~In a first variant, the layer also contains a powder of a compound of ytterbium, preferably ytterbium oxide Yb<sub>2</sub>O<sub>3</sub> or ytterbium hydroxide Y(OH)<sub>3</sub>.

[22] The active layer advantageously also contains polymer fibresfibers, such as for example polypropylene fibresfibers. These fibresfibers preferably have a length of 0.1 mm to 1.5 mm and a diameter of ~~between~~10 µm ~~and~~to 30 µm. These fibresfibers are intended to ~~strengthen~~increase the mechanical behaviourstrength of the electrode.

[23] By two-dimensional support is meant a flat support to which a paste is applied which, once dried, will form the active layer. The properties of the binder are thus essential in order to keep the active layer on the support, in particular ~~in the case of spiralling of the electrode~~for an electrode that is rolled up.

[24] The saidSaid two-dimensional conductive support ~~can~~may be a solid or a perforated strip, an expanded metal, a grid, or a fabric. It is for example a strip of nickel steel having a thickness of ~~between~~10<sup>-2</sup> mm ~~and~~to 10<sup>-1</sup> mm, with a ~~surface~~ mass of ~~between~~weight of 0.3 grams per square decimeter (g/dm<sup>2</sup>) ~~and~~to 6 g/dm<sup>2</sup>,

and with an aperture rate of between a void percentage of 0% and to 80%, the diameter of the holes being between 0.1 mm and to 3 mm.

[25] The subject of the present invention is also provides a secondary electrochemical generatorcell comprising a positive electrode, a metal-hydride negative electrode, and an aqueous alkaline electrolyte. The negative electrode ~~can~~may comprise in particular an active material ~~chosenselected~~ from cadmium and a hydrogen-fixing alloy.

#### **BRIEF DESCRIPTION OF THE DRAWING**

[26] Other characteristics and advantages of the present invention will appear duringin the following description of embodiments which are given by way of non-limiting illustration but in no way limitative.

[27] The single figure representsis a sectional view of an electrode according to of the invention.

#### **MORE DETAILED DESCRIPTION**

[28] The electrode 1 is comprisedcomprises of a plane-form conductive support 2 which fulfils the current collector function-of current collector. The support 2 is covered by an electrochemically active layer 3 which contains the electrochemically active material and a binder.

#### **EXAMPLE 1**

[29] A first electrode (1) according to of the invention iswas produced, the composition by weight of its active layer being:

[30]	Electrochemically active material based on Ni(OH) <sub>2</sub>	87.2%
[31]	Conductive material : Co(OH) <sub>2</sub> powder	10%
[32]	Styrene-acrylate copolymer	2%

[33] Cellulose compound: CMC 0.3%

[34] Y<sub>2</sub>O<sub>3</sub> 0.5%

[35] The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. The viscosity of the paste iswas adjusted with water. The paste iswas homogeneously deposited simultaneously on both sides of a two-dimensional metal support which is a ~~perforated nickel steel strip~~ in the form of a 50 µm thick perforated nickel steel strip. The whole is then dried in order to eliminate the water, then laminatedrolled to the desired thickness, and cut in order to obtain a positive electrode. Once the electrode iswas finished, the active layer displayed a porosity of 30% and a grammage of 16 g/dm<sup>2</sup>.

## EXAMPLE 2

[36] A first comparative electrode (A1) iswas produced, with an active layer having the following composition by weight:

[37] Electrochemically active material based on Ni(OH)<sub>2</sub> 88.2%

[38] Conductive material : Co(OH)<sub>2</sub> powder 10%

[39] Binder: polytetrafluoroethylene (PTFE) 1%

[40] Cellulose compound: CMC 0.3%

[41] Y<sub>2</sub>O<sub>3</sub> 0.5%

[42] The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. The viscosity of the paste iswas adjusted with water. The paste iswas introduced into a three-dimensional support comprising which is a nickel foam with a porosity of about 95%. The whole iswas then dried in order to eliminate the water, then laminatedrolled to the desired thickness and cut in order to obtain a positive electrode.

Once the electrode ~~is was~~ finished, the active layer ~~displays displayed~~ a porosity of 30% and a ~~grammagem weight~~ of 16 g/dm<sup>2</sup>.

#### EXAMPLE 3

[43] An electrode (II) ~~according to of~~ the invention ~~is was~~ produced in the manner described in Example 1, with an active layer having the following composition by weight:

[44]	Electrochemically active material based on Ni(OH) <sub>2</sub>	86.9%
[45]	Conductive material : Co(OH) <sub>2</sub> powder	10%
[46]	Styrene-acrylate copolymer	2%
[47]	Cellulose compound: CMC	0.3%
[48]	Polypropylene <del>fibres</del> <ins>fibers</ins>	0.3%
[49]	Y <sub>2</sub> O <sub>3</sub>	0.5%

[50] The powdery electrochemically active material ~~is comprised of~~ a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode ~~is was~~ finished, the active layer ~~displays displayed~~ porosity of 30% and a ~~grammagem weight~~ of 16 g/dm<sup>2</sup>.

#### EXAMPLE 4

[51] A second comparative electrode (A2) ~~is was~~ produced in the manner described in Example 2, with a layer having the following composition by weight:

[52]	Electrochemically active material based on Ni(OH) <sub>2</sub>	79.9%
[53]	Conductive material : Co(OH) <sub>2</sub> powder	10%
[54]	Binder: polytetrafluoroethylene (PTFE)	1%
[55]	Cellulose compound: CMC	0.3%
[56]	Polypropylene <del>fibres</del> <ins>fibers</ins>	0.3%
[57]	Y <sub>2</sub> O <sub>3</sub>	0.5%

[58] The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode iswas finished, the active layer displays adisplayed porosity of 30% and a grammagemeweight of 16 g/dm<sup>2</sup>.

#### EXAMPLE 5

[59] An electrode (III) according to of the invention iswas produced in the manner described in Example 1, with an active layer having the following composition by weight:

[60]	Electrochemically active material based on Ni(OH) <sub>2</sub>	86.3%
[61]	Conductive material : Co(OH) <sub>2</sub> powder	10%
[62]	Styrene-acrylate copolymer	2.9%
[63]	Cellulose compound: CMC	0.3%
[64]	Y <sub>2</sub> O <sub>3</sub>	0.5%

[65] The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode iswas finished, the active layer displays adisplayed porosity of 30% and a grammagemeweight of 16 g/dm<sup>2</sup>.

#### EXAMPLE 6

[66] An electrode (IV) according to of the invention iswas produced in the manner described in Example 1, with an active layer having the following composition by weight:

[67]	Electrochemically active material based on Ni(OH) <sub>2</sub>	84.9%
[68]	Conductive material : Co(OH) <sub>2</sub> powder	10%
[69]	Styrene-acrylate copolymer	4%
[70]	Cellulose compound: CMC	0.3%

- [71] Polypropylene fibres 0.3%
- [72] Y<sub>2</sub>O<sub>3</sub> 0.5%
- [73] The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode iswas finished, the active layer displays adisplayed porosity of 30% and a grammage of weight of 16 g/dm<sup>2</sup>.

#### EXAMPLE 7

[74] An electrode (IV) according to of the invention iswas produced in the manner described in Example 1, with an active layer having the following composition by weight:

- |      |   |        |
|------|---|--------|
| [75] | Electrochemically active material based on Ni(OH) <sub>2</sub>  | 88.75% |
| [76] | Conductive material : Co(OH) <sub>2</sub> powder  | 10%    |
| [77] | Styrene-acrylate copolymer  | 0.15%  |
| [78] | Cellulose compound: CMC   | 0.3%   |
| [79] | Polypropylene fibresfibers  | 0.3%   |
| [80] | Y <sub>2</sub> O <sub>3</sub>   | 0.5%   |
| [81] | The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode iswas finished, the active layer displays adisplayed porosity of 30% and a grammage weight of 16 g/dm <sup>2</sup> . |        |

[82] Ni-MH accumulators arestorage cells were assembled, including respectively the previously manufactured electrodes A1, A2 and I to V. TheTheir negative electrodes ofwere of known type hashaving as their electrochemically active material an intermetallic compound capable of forming a hydride once charged. Its Negative electrode capacity iswas greater than that of the positive electrode capacity.

Each positive electrode ~~is~~was placed beside a negative electrode from which it ~~is~~was isolated by a separator ~~comprised by~~comprising a nonwoven polypropylene fabric in order to form the electrochemical ~~bundle~~stack. The ~~thus spiralled bundle is~~stack was rolled up and inserted in a metal cup and impregnated with an alkaline electrolyte, which ~~is~~was an aqueous alkaline solution ~~comprised~~comprising of a mixture of potassium hydroxide KOH 7.5 N potassium hydroxide KOH, sodium hydroxide NaOH 0.4 N and lithium hydroxide LiOH 0.5 N 0.4 N sodium hydroxide NaOH, and 0.5 N lithium hydroxide LiOH.

[83] After a 48 hour ~~rest~~resting at ambient temperature for 48 hours (h), an electric formation of the accumulators is carried out under the following conditionsthe storage cells were formed electrically under the following conditions:

[84] Cycle 1: rest 2 h at 85°C;  
 charge at 0.1 lc for 4 h at 85°C, where lc is the current ~~necessary~~needed to discharge the nominal capacity C of the ~~generator~~cell in 1 h;  
 rest 2 h at 20°C;  
 charge 3 h at 0.33 lc;  
discharge at 0.2 lc to a voltage of 0.9 Vvolts  
(V);  
charge 40 minutes (min) at 1C1c, then 1 h 30 min at 0.5 lc;  
discharge at 0.2 lc to a voltage of 0.9 V.

[85] Cycles 2 to 10: charge 16 h at 0.1 lc;  
discharge at 0.2 lc to a voltage of 0.9 V;

[86] Cycle 11: charge 72 minutes at 1c;  
discharge at lc to a voltage of 0.9 V.

[87] The mass specific capacities in cycle 11, relative to the mass of coated material, are listed in Table 1 below.

[88] A mechanical behaviourstrength test of the electrodes A1, A2 and I to V was then carried out as follows: each electrode was weighed, then released from a height of 50 centimeters (cm) onto a plane surface. The drop was repeated 10 times. Then the electrode was weighed again. The result of the test is expressed as the ratio of the initial mass lessminus the final mass relative to divided by the initial mass. The smaller this ratio, the more solid an electrode will be stronger the electrode. The results obtained are shown in Table 1 below.

[89] The two comparative electrodes A1 and A2 with three-dimensional supports differ only in the presence in the active layer of polymer fibresfibers, the role of which is to strengthenincrease the mechanical behaviourstrength of the electrode. TheThese two electrodes behavebehaved in the same way during the mechanical behaviourstrength test. It isshould be noted that the mass specific capacity was identical for the twoboth comparative electrodes A1 and A2: the presence of 0.3% by weight of fibresfibers in the active layer doesdid not influence the electrochemical performance of the generatorcell.

[90] Similarly, electrodes I and II according to the present invention with two-dimensional support differ only in the presence of polymer fibresfibers in the active layer. The capacity obtained in cycle 11 was of the same order for the twoboth electrodes I and II, but it can be seen that electrode II hashad a better mechanical behaviourstrength than electrode I. The presence of 0.3% by weight of fibresfibers in the layer doesdid not influence the electrochemical performance of the generatorcell.

[91] The electrochemical evaluation of the generatorscells assembled with electrodes according to the invention shows that electrodes I and II, each including a two-dimensional conductive support and a binder according to the invention,

present a mass specific capacity at least equal to that of electrodes A1 and A2 with three-dimensional support.

[92] For a greater proportion of styrene-acrylate copolymer (electrode III) the capacity of the electrode reduces slightly. However, the increase in the proportion of binder permitted an improvement in the mechanical behaviourstrength of the electrode despite the absence of fibresfibers.

[93] If the proportion of styrene-acrylate polymer is further increased (electrode IV), the mass specific capacity of the electrode falls because of the reduction in the quantity of active material.

[94] Electrode V including a smaller proportion of styrene-acrylate copolymer displays a good mass specific capacity, but its degraded mechanical behaviourstrength makes it more difficult to use.

TABLE 1

electrode	A1	A2	I	II	III	IV	V
support	foam	foam	strip	strip	strip	strip	strip
styrene-acrylate copolymer %)	1% PTFE	1% PTFE	2	2	2.9	4	0.15
cellulose compound CMC (%)	0.3	0.3	0.3	0.3	0.3	0.32	0.3
polypropylene fibresfibers (%)	0.3	-	-	0.3	-	0.3	0.3
mechanical behaviourstrength of the electrode (%)	0.2	0.2	1	0.2	0.3	0.15	5.1
generated cell output in cycle 11 (milliampere-hours per gram) (mAh/g)	239	240	242	245	235	220	244